

FINAL TECHNICAL REPORT

RAMAN SPECTROSCOPIC STUDIES OF CARBON

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RESEARCH SUMMARY

The measurements obtained in this work indicate ways in which micro-Raman spectroscopy can be used to elucidate structural characteristics and distribution of carbon in meteorites and interplanetary dust particles (IDPs). Existing information about structurally significant aspects of Raman measurements of graphite (Lespade, *et al.*, 1984 and Vidano and Fishbach, 1978) is combined with structurally relevant findings from the present micro-Raman studies of carbons prepared by carbonization of polyvinylidene chloride (PVDC) at various temperatures (Ban, *et al.*, 1975) and natural material, as well as several acid residues, from the Allende and Murchison meteorites in order to establish new spectra-structure relationships. Structural features of many of the materials in this study have been measured by X-ray analysis and electron microscopy; thus, their structural differences can be directly correlated with differences in the Raman spectra. The spectral parameters consequently affirmed as indicators of structure are used as a measure of structure in materials that have unknown carbon structure, especially IDPs.

The unique applicability of micro-Raman spectroscopy is realized not only in the ability to conveniently measure spectra of micron-sized IDPs, but also micron-sized parts of an inhomogeneous material. For example, Raman measurements at visibly distinct features across a microtomed section of an Allende meteorite sample give similar carbon spectra and various bands attributable to mineral suggesting that the structure of carbon in the sample is uniform and independent of its environment. Another example is given by measurements of bright appearing microcrystalline regions of a Murchison acid residue. An unusual sharp band is sometimes observed between 1300 and 1350 cm^{-1} in these spectra that can be assigned as due to diamond. This feature could not be observed in bulk measurement. Moreover, micro-Raman spectra can be correlated with other micro-measurements at the same position on the sample.

Microcrystalline graphite is known to give Raman spectra that differ dependent on crystallite size (see e.g., Lespade, *et al.*, 1984, or Nemanich and Solin, 1979). The spectral changes that accompany decreasing particle size include increase in the ratio (R) of the intensity of the band near 1350 cm^{-1} (D band) to that of the band near 1600 cm^{-1} (G band) increase in the half width of the D band (wD) increase in the frequency maximum of the G band and increase in the half width (wG) of the 2nd order band near 2700 cm^{-1} (G') band.

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RAMAN SPECTRA OF CARBON

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In addition, the current Raman Measurements of Allende, Murchison and PVDC carbons include changes that accompany variation of the Raman excitation frequency and heat treatment temperature (HTT) of the sample and yield new indications of carbon structure that are applicable to structural interpretation of non-graphitic carbons. The value of R decreases and the frequencies of the D and G' bands increase as a function of increasing Raman excitation frequency (Vidano, *et al*, 1981). These changes have not been satisfactorily explained but are likely due to differences in resonance Raman enhancement. The values and changes are dependant upon structure and can be included in observations that indicate structure. Changes in the Raman spectra of most carbon containing materials with successively higher HTT can be related to changes in the structure of the carbon with increasing HTT and the structure before heating. For example, an increase in R and the intensity of the G' and 2920 cm^{-1} bands with heating is shown to accompany the formation of non-planar trigonal carbon layers, and decrease in R and intensity at 2920 cm^{-1} while the intensity of the G' band increases signals the increase of planar trigonal carbon layers with D_{6h} symmetry. The structure that is developed with increased HTT depends upon the structure and distribution of carbon in the precursor material. It is clear from these results that R in spectra of non-graphitic carbon materials depends upon factors other than crystallite size.

Upon subjecting carbon from the Allende meteorite to successively high HTT, R is decreased while Murchison carbon gives an increase in R with higher HTT. The R in spectra of PVDC carbons increases with higher HTT. These observations along with comparison of R , wD , wG' , the frequency of the G band and the intensities of the G' band and that at 2920 cm^{-1} with corresponding parameters given by the structurally characterized PVDC carbons. (Ban, *et al.*, 1975) suggest that the carbon in Allende is primarily non-planar layers of trigonal carbon that forms more planar graphitic material upon being heated and that carbon in Murchison is largely poorly developed crosslinked carbon polymer that forms more non-planar layers of trigonal carbon with higher HTT. The more uniform and well developed structure of Allende carbon and the opposing spectral changes with increased HTT relative to Murchison suggest that the carbon structures in Allende and Murchison result from different formation mechanisms and/or that the Allende meteorite has experience a much higher temperature than Murchison. The IDPs that are included in this study give spectra that are very much like those given by Murchison carbon. They likely contain carbon that is similar in structure or have even fewer crosslinks than that in the Murchison meteorite.

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FINAL DISCLOSURE OF INVENTIONS

No inventions resulted from the work carried out under this contract.

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